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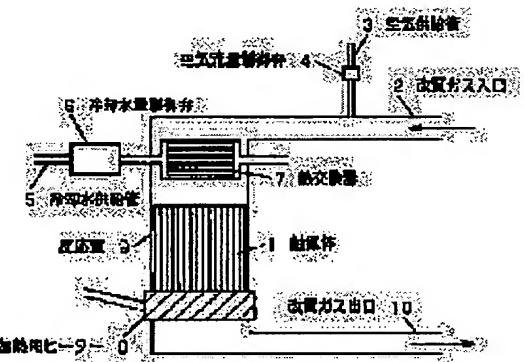
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(54) HYDROGEN PURIFYING DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To oxidize and remove carbon monoxide with high selectivity and to stably operate temp. control by providing a catalyst layer on the downstream side of the supply part of a reformed gas and the supply part of an oxygen- contg. gas providing a cooling means on the upstream side of the catalyst with and providing a heating means on the downstream side of the catalyst.

SOLUTION: When a fuel is reformed with steam, the concn. of carbon monoxide increases. When a fuel is reformed at $\leq 300^{\circ}\text{C}$ such as methanol, the concn. of carbon monoxide becomes about 1%. This reformed gas is introduced through a reformed gas inlet 2 of a hydrogen purifying device. Since a reformed gas of methane or natural gas contains carbon monoxide by $\geq 10\%$, the gas is reacted with steam by a modified catalyst to convert carbon monoxide into carbon dioxide and hydrogen and to decrease the concn. of carbon monoxide to $\leq 1\%$. Then the gas is introduced through the reformed gas inlet 2. Air is introduced through and air supply tube 3 and reacted in the catalyst layer 1 to oxidize the carbon monoxide in the reformed gas. The reformed gas mixed with air is cooled to the activating temp. of the catalyst by a heat exchanger 7, and the gas temp. is gradually increased as it goes to the downstream side.



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CLAIMS

[Claim(s)]

[Claim 1] The hydrogen refiner characterized by to have a cooling means cool the catalyst object provided in the downstream of the feed zone of the reformed gas which uses hydrogen gas as a principal component and contains a carbon dioxide and a carbon monoxide, the feed zone of oxygen content gas, and the feed zone of said reformed gas and the feed zone of said oxygen content gas, said catalyst object with which the upstream of said catalyst object was equipped to the flow direction of said reformed gas, or said reformed gas, and a heating means heat the downstream of said catalyst object.

[Claim 2] A catalyst object is a hydrogen refiner according to claim 1 characterized by constituting the upstream and the downstream from a catalyst of another kind, and the catalyst of the downstream having activity at low temperature rather than the catalyst of the upstream.

[Claim 3] The hydrogen refiner according to claim 1 or 2 characterized by having arranged the catalyst object to two or more places, and installing the air supply section separately to said catalyst object.

[Claim 4] A catalyst object is a hydrogen refiner according to claim 1, 2, or 3 characterized by supporting a catalyst to the support base material of the foam structure of having honeycomb structure or a free passage hole.

[Claim 5] A support base material is a hydrogen refiner according to claim 4 characterized by being a metal base.

[Claim 6] A heating means is a hydrogen refiner according to claim 1, 2, 3, 4, or 5 characterized by using heat of reaction with the carbon monoxide in reformed gas, hydrogen, and the oxygen in oxygen content gas.

[Claim 7] The hydrogen refiner according to claim 1, 2, 3, 4, 5, or 6 characterized by making downstream temperature of a catalyst object into an elevated temperature rather than the upper section.

[Claim 8] The hydrogen refiner according to claim 7 characterized by changing the amount of supply of oxygen content gas corresponding to the temperature rise of a catalyst object.

[Claim 9] The hydrogen refiner according to claim 1, 2, 3, 4, or 5 characterized by using for heating of the downstream of said catalyst object reformed gas before installing a catalyst object in a reaction chamber, installing reformed gas passage in the location approached or stuck through the septum with said catalyst object and passing a cooling means.

[Claim 10] The hydrogen refiner according to claim 9 considered as the configuration which the flow of the reformed gas which passes a catalyst object, and said reformed gas before passing a cooling means counters mutually.

[Claim 11] The hydrogen refiner according to claim 9 or 10 characterized by installing a reaction chamber in the periphery section of the reformed gas passage before passing a catalyst object.

[Claim 12] The hydrogen refiner according to claim 10 or 11 characterized by having installed the catalyst object in the interior of the reaction chamber which has the tubular structure, and installing the passage of reformed gas before passing a cooling means in the periphery section of said reaction chamber.

[Claim 13] The hydrogen refiner according to claim 12 characterized by connecting two or more

reaction chambers to juxtaposition.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention uses as a principal component the hydrogen used for fuels, such as a fuel cell, and relates to the hydrogen refiner in the reformed gas containing a carbon dioxide and the carbon monoxide of a minute amount which carries out carbon monoxide removal.

[0002]

[Description of the Prior Art] A fuel cell uses the reformed gas obtained by reforming of a hydrocarbon or alcohol as a source of hydrogen. Poisoning of the polymer electrolyte fuel cell which operates at low temperature 100 degrees C or less among fuel cells is carried out with the carbon monoxide with which the platinum catalyst used for an electrode is included in reformed gas. If poisoning of the platinum catalyst is carried out, in order for the generating efficiency of a fuel cell to fall remarkably, it is necessary to remove preferably 100 ppm or less of carbon monoxides to 10 ppm or less. Then, oxygen content gas is mixed to reformed gas, and the method of removing the carbon monoxide of the minute amount contained in the hydrogen of an overlarge is taken using the catalyst which oxidizes a carbon monoxide alternatively. In order to remove a carbon monoxide efficiently, the catalyst needed to be held to optimum temperature, but rather than the optimum temperature of a carbon monoxide selective oxidation reaction, since reformed gas was an elevated temperature, it needed to cool, before usually supplying a carbon monoxide to the catalyst which carries out selective oxidation, and it needed to be adjusted to optimum temperature.

[0003]

[Problem(s) to be Solved by the Invention] The amount of oxygen is made [whether it is the same as the amount of carbon monoxides, and] into about several times at the reaction which carries out selective oxidation of the carbon monoxide in reformed gas. At this time, if oxygen is consumed by oxidation of the hydrogen which exists so much in reformed gas, only a part with insufficient oxygen will be discharged by it, without a carbon monoxide reacting. At this time, the rate of the oxygen used for oxidation of a carbon monoxide becomes high, so that reaction temperature becomes low temperature. However, if it becomes below the catalytic activity-ized temperature that can oxidize a carbon monoxide, it will be discharged, without a carbon monoxide reacting. Then, it is necessary to control whenever [catalyst temperature] to the temperature field to which a carbon monoxide reacts and the reaction of hydrogen seldom occurs.

[0004] The temperature which can oxidize a carbon monoxide efficiently most is the temperature of the low-temperature limitation that the reaction of a carbon monoxide occurs. However, when the temperature control of the selective oxidation catalyst of a carbon monoxide is controlled only for cooling of the reformed gas to supply or a catalyst object to come out, a vast quantity of carbon monoxides are discharged only by temperature falling slightly. For this reason, in consideration of temperature fluctuation of the flow rate of reformed gas, or a catalyst object, it controls by the temperature field high about dozens of degrees C from several degrees C rather than a low-temperature limitation. Thereby, the selectivity of carbon monoxide oxidation by the conventional approach was

low.

[0005]

[Means for Solving the Problem] This invention can carry out oxidation removal of the carbon monoxide in high selectivity in consideration of the technical problem of such a hydrogen refiner, and it is easy and temperature control aims at offering the hydrogen refiner which operates to stability. Therefore, the feed zone of the reformed gas which the hydrogen refiner of this invention uses hydrogen gas as a principal component, and contains a carbon dioxide and a carbon monoxide, The catalyst object provided in the downstream of the feed zone of oxygen content gas, and the feed zone of said reformed gas and the feed zone of said oxygen content gas, Water characterized by having a cooling means to cool said catalyst object with which it prepared for the upstream of said catalyst object to the flow direction of said reformed gas, or said reformed gas, and a heating means to heat the downstream of said catalyst object.

[0006] As for a catalyst object, at this time, it is effective that constitute the upstream and the downstream from a catalyst of another kind, and the catalyst of the downstream has activity at low temperature rather than the catalyst of the upstream.

[0007] Moreover, it is effective to have arranged the catalyst object to two or more places, and to have installed the air supply section separately to said catalyst object.

[0008] Moreover, as for a catalyst object, it is useful to have supported the catalyst to the support base material of the foam structure of having honeycomb structure or a free passage hole.

[0009] As for a support base material, at this time, it is useful that it is a metal base. Moreover, as for a heating means, it is effective to use heat of reaction with the carbon monoxide in reformed gas, hydrogen, and the oxygen in oxygen content gas.

[0010] At this time, it is effective to make downstream temperature of a catalyst object into an elevated temperature rather than the upper section. Moreover, it is effective to change the amount of supply of oxygen content gas corresponding to the temperature rise of a catalyst object.

[0011] Moreover, a catalyst object is installed in a reaction chamber and, as for said catalyst object, it is effective to use for heating of the downstream of said catalyst object reformed gas before installing reformed gas passage in the location approached or stuck through the septum and passing a cooling means.

[0012] At this time, the flow of the reformed gas which passes a catalyst object, and said reformed gas before passing a cooling means considered as the configuration which counters mutually.

[0013] Moreover, it is characterized by installing a reaction chamber in the periphery section of the reformed gas passage before passing a catalyst object.

[0014] Furthermore, it is characterized by having installed the catalyst object in the interior of the reaction chamber which has the tubular structure, and installing the passage of reformed gas before passing a cooling means in the periphery section of said reaction chamber.

[0015] Moreover, it is characterized by connecting two or more reaction chambers to juxtaposition.

[0016]

[Embodiment of the Invention] In order to solve the above-mentioned technical problem, while having a means to cool a catalyst object or reformed gas to the upstream of a catalyst object to the flow direction of reformed gas, with the hydrogen refiner of this invention, it is characterized by having a means to heat the downstream of a catalyst object. Moreover, it is characterized by using the heat of combustion of a carbon monoxide and hydrogen, or the reformed gas before cooling for heating at heating of a catalyst object downstream.

[0017] According to this invention, temperature control becomes remarkably easy, while being stabilized and being able to operate a carbon monoxide selective oxidation catalyst.

[0018] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. (Gestalt 1 of operation) Drawing 1 is the configuration schematic drawing of the hydrogen refiner which is the gestalt of operation of the 1st of this invention. drawing 1 -- setting -- 1 -- a catalyst object and 2 -- a reformed gas inlet port and 3 -- air supply tubing and 4 -- for a circulating water flow control valve and 7, as for the heater for heating, and 9, a heat exchanger and 8 are [an air flow control valve and 5 / a

cooling water supply pipe and 6 / a reaction chamber and 10] reformed gas outlets.

[0019] Next, actuation and the property of the gestalt of this operation are explained. When steam reforming of the fuel is carried out, carbon monoxide concentration rises, so that reaction temperature becomes high. In reforming below 300 degrees C like a methanol, since carbon monoxide concentration becomes about 1%, it introduces reformed gas from the direct reformed gas inlet port 2. On the other hand, the methane which a reaction takes the temperature of about 600 degrees C, or the reformed gas of natural gas is introduced from the reformed gas inlet port 2, after making it react with a steam according to a conversion catalyst, converting into a carbon dioxide and hydrogen and reducing carbon monoxide concentration to 1% or less in this way, since the carbon monoxide is included 10% or more from the balance of a water gas shift reaction.

[0020] In order to oxidize the carbon monoxide in reformed gas, air is introduced and it is made to react with the catalyst object 1 from the air supply tubing 3. If there are few air contents, a carbon monoxide will not react enough, but since the consumption of hydrogen will increase if there are many air contents conversely, the air content supplied by the air flow control valve 4 is adjusted so that 1 to 3 times as much oxygen as a carbon monoxide may be contained by the volume ratio. It is cooled to less than [the temperature to which catalytic activity, the activation temperature, i.e., the carbon monoxide, of a catalyst, begins to decrease rapidly by the heat exchanger 7, or it], and the reformed gas which mixed air is supplied to the catalyst object 1.

[0021] Here, what supported platinum to the alumina is coated and used for the ceramic honeycomb, and a property like drawing 2 is shown in the catalyst object 1. That is, in order that the carbon monoxide in reformed gas may react at low temperature rather than hydrogen, the carbon monoxide concentration discharged, so that whenever [catalyst temperature] is made into low temperature falls. If temperature is furthermore reduced, since it will be less than the activation temperature of a catalyst, the carbon monoxide concentration which a carbon monoxide will not react, either and is discharged increases rapidly.

[0022] Since the temperature of the catalyst object 1 is controlled so that temperature rises as the upper section of the catalyst object 1 is made to become near the activation temperature of a catalyst, or below activation temperature in a cooling operation of a heat exchanger 7 and it goes to a downstream, the band of temperature where a carbon monoxide reacts most efficiently on the catalyst object 1 can be made. In this way, the carbon monoxide in reformed gas can be reduced to several ppm level which is the concentration to which the property of a polymer electrolyte fuel cell is not reduced. At this time, a carbon monoxide is removable to stability only by the location of the band of temperature where a carbon monoxide reacts most efficiently moving to the upstream or the downstream, even if reformed gas and a cooling system have some temperature fluctuation.

[0023] With the gestalt of this operation, although air was used as oxygen content gas, if pure oxygen is used, only the part in which the fall of the hydrogen concentration of reformed gas does not contain nitrogen will be eased, and the generating efficiency of the fuel cell which connects behind will rise. However, it is [having usually used air direction-wise / cost] advantageous.

[0024] Moreover, although the electric heater was used for heating of the catalyst object 1 in this example, it is good also as a heating means of the downstream of the catalyst object 1 using the heat of combustion of a carbon monoxide and hydrogen. The temperature distribution of the catalyst object 1 can be made the optimal with the minimum heater heating, without using an electric heater etc. by adjusting the flow rate of the reformed gas which passes the catalyst object 1, and the rate of air, and using the heat of combustion of a carbon monoxide and hydrogen.

[0025] Moreover, since the heat of combustion of CO and hydrogen increases in proportion to an air content, the temperature of the catalyst object 1 can also be maintained at a suitable condition by adjusting an air content, and the catalyst object 1 can be operated more as stability by this approach.

[0026] Moreover, a metal base may be used although the cordierite honeycomb was used for the support base material of the catalyst object 1. Since heat of reaction can be promptly missed by using a metal base for a support base material, control of the temperature rise by the heat of combustion of a carbon monoxide and hydrogen is possible. Therefore, while being able to raise the reformed gas throughput

per unit volume of the catalyst object 1, the effect of the heat-of-reaction increase and decrease by the load effect is also eased, and a stable property is acquired.

[0027] (Gestalt 2 of operation) The gestalt of operation of the 2nd of this invention is explained. As shown in drawing 3, the hydrogen refiner of this example installs the catalyst object 11 of a honeycomb configuration in the interior of the tubing-like reaction chamber 18, and establishes the passage of reformed gas in the outside of a reaction chamber 18, the fin 20 for heat exchange is formed in the wall surface of the reformed gas passage which touches the downstream of the catalyst object 11, and the great portion of operation effectiveness is similar to the gestalt 1 of operation. Therefore, this example is explained focusing on a different point.

[0028] Drawing 3 is the cross-section block diagram of this example. While being able to heat the downstream of the catalyst object 11 by approaching the perimeter side attachment wall of the downstream of the catalyst object 11, and forming the fin 20 for heat exchange, reformed gas can be cooled and cooling by the heat exchanger 17 becomes easy. Moreover, since the passage of reformed gas keeps the catalyst object 11 warm, the temperature distribution of the core of the catalyst object 11 and the periphery section are equalized, and a carbon monoxide can be oxidized efficiently. Moreover, since it constitutes so that the flow of the reformed gas which passes the catalyst object 11, and reformed gas before passing a heat exchanger 17 may counter, hot reformed gas carries out heat exchange to the downstream of the catalyst object 1, and since the cooled reformed gas passes through the side face of the catalyst object upstream section, it is low in the upper section temperature of the catalyst object 1, downstream temperature can be made high, and it can be made the optimal temperature distribution to the selective oxidation of a carbon monoxide.

[0029] Although this example showed the example the number of reaction chambers 18 is [example] one, two or more reaction chambers 18 can also be formed. By forming two or more reaction chambers 18, the effectiveness of heat exchange with reformed gas can be raised, and it can respond also to large capacity-ization.

[0030] (Gestalt 3 of operation) The hydrogen refiner which is the gestalt of operation of the 3rd of this invention is explained. As shown in drawing 4, this example establishes a reaction chamber 28 in the periphery of tubing-like reformed gas passage, and installs the catalyst object 21 of a honeycomb configuration in the interior of a reaction chamber 28, the fin 30 for heat exchange is formed in the wall surface of the reformed gas passage which touches the downstream of the catalyst object 21, and the great portion of operation effectiveness is similar to the gestalt 2 of operation. Therefore, this example is explained focusing on a different point.

[0031] Drawing 4 is the cross-section block diagram of the hydrogen refiner of this example. While being able to heat the downstream of the catalyst object 21 by forming the fin 30 for heat exchange in the downstream of the catalyst object 21, and the wall surface of the approaching reformed gas passage, reformed gas can be cooled and cooling by the heat exchanger 27 becomes easy. Moreover, when enlarging the flow rate of reformed gas and the temperature rise by the heat of combustion of a carbon monoxide and hydrogen is large, it may sometimes be insufficient only by cooling by the heat exchanger. Since the temperature rise of the catalyst object 21 can be controlled by considering as the configuration made to radiate heat from the periphery section of a reaction chamber 38, it can respond, also when the flow rate of reformed gas is made to increase and a load is enlarged.

[0032] (Gestalt 4 of operation) The gestalt of operation of the 4th of this invention is explained. The hydrogen refiner of this example installs the second catalyst object 32 in the interior of a reaction chamber 40 at the downstream of the first catalyst object 31 of a honeycomb configuration, and the first catalyst object 31, as shown in drawing 5, and the great portion of operation effectiveness is similar to the gestalt 1 of operation. Therefore, the gestalt of this operation is explained focusing on a different point.

[0033] Drawing 5 is the cross-section block diagram of the hydrogen refiner of this example. The temperature fields where a carbon monoxide selection catalyst functions according to the noble-metals kind included in a catalyst, the class of support, etc. differ. A low-temperature-service catalyst is used for the second catalyst object 32 at the first catalyst object 31 using a high-temperature-service catalyst.

Specifically, what supported platinum to the alumina at the second catalyst object 32 was used for the first catalyst object 31 using what supported platinum to the zeolite.

[0034] As shown in drawing 6, at an elevated temperature, the high-temperature-service catalyst used for the first catalyst object 31 oxidizes a carbon monoxide with high selectivity, in low temperature, does not react but passes unreacted oxygen with a carbon monoxide. Therefore, at an elevated temperature, since oxygen is not supplied to the second catalyst object 32, it does not participate in a reaction at all. On the other hand, at low temperature, since a carbon monoxide and oxygen pass the first catalyst object 31, the second catalyst object 32 can mainly function and a carbon monoxide can be removed. Moreover, with the heat of reaction in the second catalyst object 32, the downstream of the first catalyst object 31 can be heated and the temperature distribution of the first catalyst object 31 can be changed into the optimal condition. Thus, a catalyst object can be operated in a large temperature requirement by arranging two or more catalyst objects which function in a different temperature field.

[0035] Although this example showed the example which arranged the catalyst object of the honeycomb configuration of two pieces, three or more catalyst objects may be arranged. By arranging much catalyst objects, a carbon monoxide is efficiently removable in a large temperature requirement.

[0036] Moreover, the first catalyst object 31 and the second catalyst object 32 may not be separated, but you may make it the unified configuration. When especially the catalyst object of a pellet type is used by really constituting, inclusion to equipment becomes easy.

[0037] Moreover, the catalyst which a carbon monoxide is made to react to the second catalyst object 32 with hydrogen, and methanates may be used. When it controls by the first catalyst object 31 to the temperature which consumes all oxygen, since the carbon monoxide which remained does not have oxygen, it cannot oxidize with the second catalyst object 32. By using for the second catalyst object 32 the catalyst which methanates a carbon monoxide, a carbon monoxide can be made to be able to react with hydrogen and it can convert into methane. Moreover, since the methanation reaction of a carbon monoxide tends to advance at an elevated temperature rather than a carbon monoxide selective oxidation reaction, it is desirable to install the heater 39 for heating in the downstream of the second catalyst object like this example.

[0038] (Gestalt 5 of operation) The gestalt of operation of the 5th of this invention is explained. As shown in drawing 7, the hydrogen refiner of this example installs the second catalyst object 52 in the interior of a reaction chamber 62 at the downstream of the first catalyst object 51 of a honeycomb configuration, and the first catalyst object 51, and installs the second air supply tubing 55 between the first catalyst object 51 and the second catalyst object 52, and the great portion of operation effectiveness is similar to the gestalt 1 of operation. Therefore, this example is explained focusing on a different point.

[0039] Drawing 7 is the cross-section block diagram of the hydrogen refiner of this example. A high-temperature-service catalyst is used for the second catalyst object 52 at the first catalyst object 51 using a low-temperature-service catalyst. With the first catalyst object 51, when the temperature rise by the reaction is large, the selectivity of carbon monoxide oxidation sometimes falls. For this reason, the second catalyst object 52 and the second air supply tubing 55 are formed, the air supply to the first catalyst object 51 from the first air supply tubing 54 is reduced, and the temperature rise in the first catalyst object 51 is controlled. A carbon monoxide is efficiently removable with this.

[0040] Most carbon monoxides are removable with the first catalyst object 51. However, the carbon monoxide concentration discharged increases somewhat by reducing the amount of air supply compared with the case where the amount of air supply is not reduced. For this reason, the air of the amount corresponding to the carbon monoxide which remained in the second catalyst object 52 is supplied, and the remaining carbon monoxides are removed. Since the selectivity of carbon monoxide oxidation of only the part by which the temperature rise was controlled with the first catalyst object 51 improves, the total amount of the required air over the first catalyst object 51 and the second catalyst object 52 decreases. Moreover, since there is little amount of supply of the oxygen content gas to the second catalyst object 52 and the temperature rise by the heat of combustion is small, in order to maintain the second catalyst object 52 at optimum temperature, it heats at the heater 61 for heating. Thus, a carbon

monoxide is efficiently removable to stability.

[0041] Although the low-temperature-service catalyst was used for the first catalyst object 51 and the high-temperature-service catalyst was used for the second catalyst object 52 in this example, a high-temperature-service catalyst may be conversely used for the first catalyst object 51, and a low-temperature-service catalyst may be used for the second catalyst object 52. By using a high-temperature-service catalyst for the first catalyst object 51, the cooling load in a heat exchanger 60 can be reduced. Moreover, even when the temperature fall by heat dissipation between the first catalyst object 51 and the second catalyst object 52 is large by using a low-temperature-service catalyst object for the second catalyst object 52, a carbon monoxide can be removed efficiently.

[0042] As mentioned above, although the example carried out about this invention to the hydrogen refiner which used methane reformed gas and methanol reformed gas explained, as for this invention, it is needless to say that it is not what is limited to this. That is, it is contained in this invention also when as follows.

[0043] With the gestalt of this operation, other gas system hydrocarbon fuel or reformed gas of a liquid system hydrocarbon fuel, such as gasoline and kerosene, is sufficient as a propane, butane, etc.

[0044] Moreover, although what mainly supported platinum to the alumina was used for the catalyst object as a catalyst, as long as it is the catalyst which can be alternatively oxidized to a carbon monoxide, other noble metals, such as a rhodium and a ruthenium, the catalyst which made these compound-ize or a transition-metals multiple oxide with a perovskite structure, etc. may be used. Moreover, a silica alumina, a zeolite, etc. may be used instead of an alumina. Moreover, the catalyst which methanates a carbon monoxide alternatively depending on the case may be used.

[0045] Moreover, reformed gas may contact a catalyst efficiently, as long as pressure loss is the configuration which does not become not much large, the configuration of the catalyst object 1 may be spherical, or the thing of a pellet type is sufficient as it, although considered as the honeycomb configuration.

[0046] Moreover, although the approach of circulating water and carrying out heat exchange was used for cooling of reformed gas, as long as it is required, oil-like matter like the high ethylene glycol of the boiling point or these mixed liquor may be circulated with temperature. Moreover, you may use for the preheating of reforming material gas using the gas supplied to the reforming section.

[0047]

[Example] (Example 1) The cordierite honeycomb with a diameter [of 50mm] and a die length of 100mm was coated with the alumina which supported platinum, and the catalyst object 1 was produced. It installed into the reaction chamber 9 of the hydrogen refiner which shows this catalyst object 1 to drawing 1 , and the reformed gas 15%, 15% of steams, and whose remainder are hydrogen about 1% of carbon monoxides and a carbon dioxide was introduced by the flow rate of 10l./m from the reformed gas inlet port 2. Air 11./m was supplied from air supply tubing. The reformed gas with which this air was mixed was reduced to 100 degrees C to inside by the heat exchanger 7 which circulated water, and was made to react with the catalyst object 1. Using the heater 8 for heating, the downstream of the catalyst object 1 was set up so that it might become 150 degrees C. When the temperature distribution of the catalyst object 1 were measured, it applied to the downstream from the upper section, and temperature was rising almost linearly. When the presentation of the reformed gas discharged from the reformed gas outlet 10 after catalyst object 1 passage was measured by the gas chromatography, carbon monoxide concentration was 5 ppm. Moreover, when the flow rate of the water which flows the inside of a heat exchanger 7 was changed and reformed gas temperature was changed with 90 degrees C and 80 degrees C, carbon monoxide concentration was set to 6 ppm and 9 ppm, respectively. Moreover, when the laying temperature of the heating heater 8 was changed and temperature of catalyst object 1 downstream was made into 140 degrees C and 160 degrees C, carbon monoxide concentration was set to 4 ppm and 9 ppm, respectively.

[0048] (Example 2) It installed in the reaction chamber 18 which shows the catalyst object produced in the example 1 to drawing 3 , and reformed gas was introduced from the reformed gas inlet port 12. When the reformed gas temperature in the reformed gas inlet port 12 was measured, it was 200 degrees

C. When the temperature of catalyst object 11 downstream heated through the fin 20 for heat exchange was measured, it was 150 degrees C. When reformed gas was reduced to 100 degrees C by the heat exchanger 17 and it was made to react with the catalyst object 11, carbon monoxide concentration was 5 ppm.

[0049] (Example 3) As shown in drawing 4, what bored the hole with a diameter of 80mm at the core of a cordierite honeycomb with a diameter [of 100mm] and a die length of 100mm was coated with the catalyst as well as the example 1, and the catalyst object 21 was produced. When the temperature of catalyst object 11 downstream heated through the fin 30 for heat exchange was measured, it was 150 degrees C. When reformed gas was reduced to 100 degrees C by the heat exchanger 27 and it was made to react with the catalyst object 21, carbon monoxide concentration was 4 ppm.

[0050] (Example 4) The cordierite honeycomb with a diameter [of 50mm] and a die length of 50mm was coated with the alumina which coated the cordierite honeycomb with a diameter [of 50mm], and a die length of 50mm with the mordenite which supported platinum, and supported the first catalyst object 31 and platinum, and the second catalyst object 32 was produced, respectively. This first catalyst object 31 and the second catalyst object 32 were installed in the reaction chamber 40, as shown in drawing 5, respectively. It cooled to 140 degrees C by the heat exchanger 38, and reformed gas controlled the downstream of the second catalyst object 32 by the heater 39 for heating to become 160 degrees C. When the temperature of the downstream of the first catalyst object 31 was measured, it was 150 degrees C. It was 1 ppm when the carbon monoxide concentration of the reformed gas outlet 41 was measured.

[0051] (Example 5) The cordierite honeycomb with a diameter [of 50mm] and a die length of 50mm was coated with the alumina which coated the cordierite honeycomb with a diameter [of 50mm], and a die length of 50mm with the mordenite which supported platinum, and supported the first catalyst object 51 and platinum, and the second catalyst object 52 was produced, respectively. This first catalyst object 51 and the second catalyst object 52 were installed in the reaction chamber 62, as shown in drawing 7, respectively. It cooled to 150 degrees C by the heat exchanger 60, and reformed gas controlled the downstream of the second catalyst object 52 by the heater 61 for heating to become 130 degrees C. When the temperature of the downstream of the first catalyst object 51 was measured, the temperature of 140 degrees C and the second catalyst object upstream section was 100 degrees C. It was 2 ppm when the carbon monoxide concentration of the reformed gas outlet 63 was measured.

[0052] (Example 1 of a comparison) In the example 1, the heating heater 8 was removed and, similarly reformed gas was introduced from the reformed gas inlet port 2. Reformed gas temperature was reduced to 100 degrees C, and it was made to react with the catalyst object 1 by the heat exchanger 7. When the temperature distribution of the catalyst object 1 were measured, temperature fell linearly as the upper section went down-stream by 100 degrees C, and the lowest style section temperature was 90 degrees C. It was 2000 ppm when the presentation of the reformed gas discharged from the reformed gas outlet 10 after catalyst object 1 passage was measured by the gas chromatography. Moreover, when the flow rate of the water which flows the inside of a heat exchanger 7 was changed and reformed gas temperature was changed with 90 degrees C, 110 degrees C, and 120 degrees C, carbon monoxide concentration was set to 5000 ppm, 200 ppm, and 500 ppm, respectively.

[0053] (Example 2 of a comparison) In the example 5, when the heater 61 for heating was removed, and the temperature of the downstream of the first catalyst object 51 was measured, the temperature of 100 degrees C and second catalyst object 52 downstream of the temperature of 140 degrees C and the second catalyst object 52 upstream section was 90 degrees C. It was 500 ppm when the carbon monoxide concentration of the reformed gas outlet 63 was measured.

[0054]

[Effect of the Invention] Temperature control becomes remarkably easy, while according to this invention being stabilized and being able to operate a carbon monoxide selective oxidation catalyst so that clearly from the place described above.

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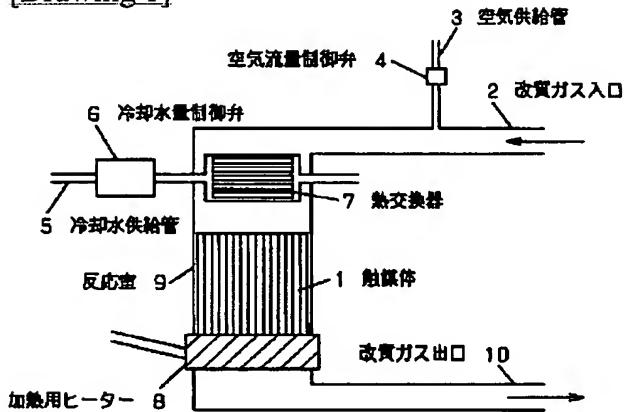
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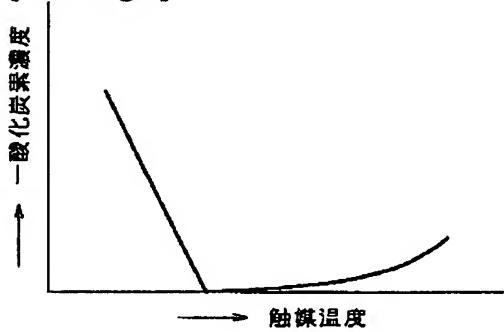
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DRAWINGS

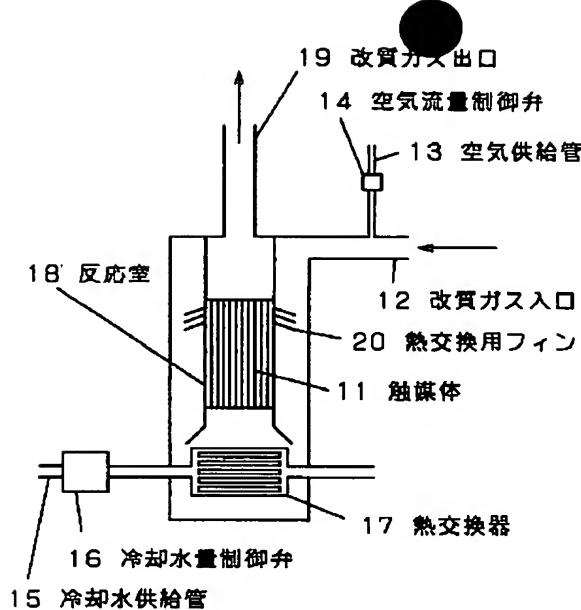
[Drawing 1]



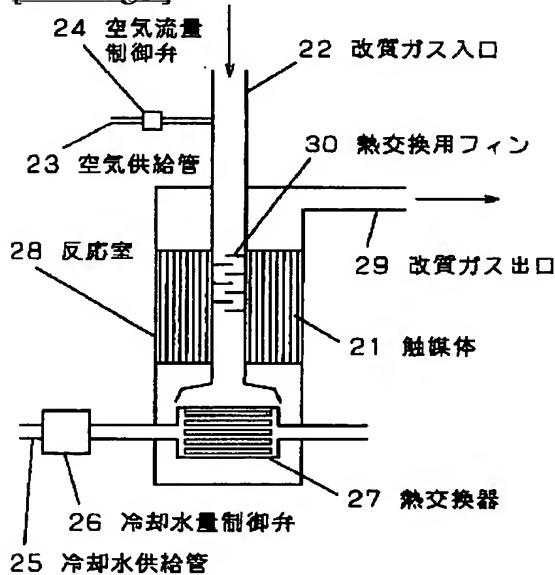
[Drawing 2]



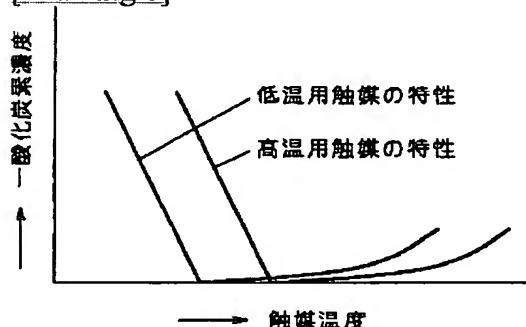
[Drawing 3]



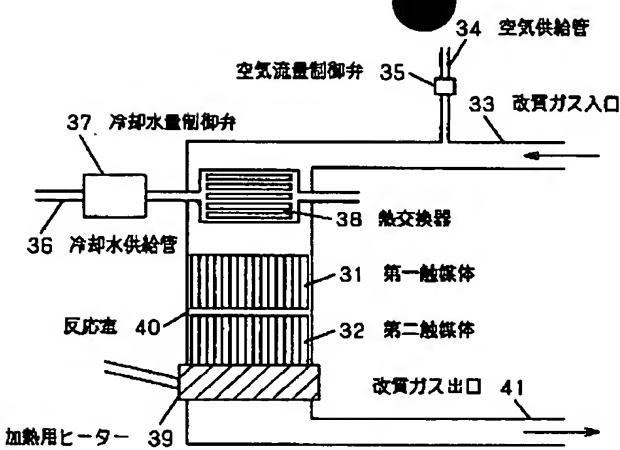
[Drawing 4]



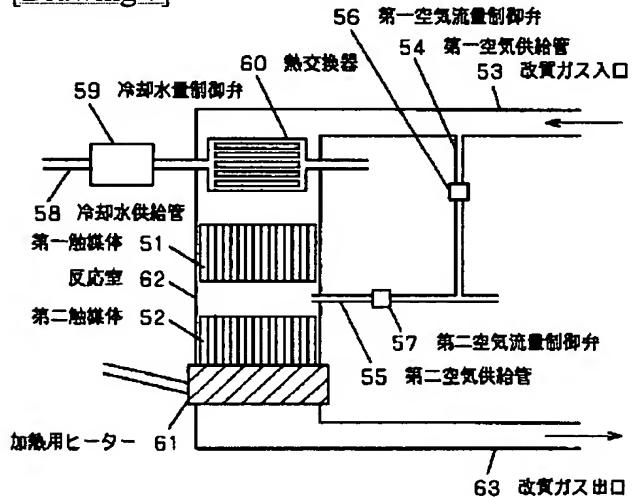
[Drawing 6]



[Drawing 5]



[Drawing 7]



[Translation done.]

* NOTICES *

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3. In the drawings, any words are not translated.

CORRECTION OR AMENDMENT

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 [Document to be Amended] Specification
 [Item(s) to be Amended] Claim
 [Method of Amendment] Modification
 [Proposed Amendment]
 [Claim(s)]
 [Claim 1] The hydrogen refiner characterized by to have a cooling means cool the catalyst object provided in the downstream of the feed zone of the reformed gas which uses hydrogen gas as a principal component and contains a carbon dioxide and a carbon monoxide, the feed zone of oxygen content gas, and the feed zone of said reformed gas and the feed zone of said oxygen content gas, said catalyst object with which the upstream of said catalyst object was equipped to the flow direction of said reformed gas, or said reformed gas, and a heating means heat the downstream of said catalyst object.
 [Claim 2] A catalyst object is a hydrogen refiner according to claim 1 characterized by constituting the upstream and the downstream from a catalyst of another kind, and the catalyst of the downstream having activity at low temperature rather than the catalyst of the upstream.
 [Claim 3] A heating means is a hydrogen refiner according to claim 1 or 2 characterized by using heat of reaction with the carbon monoxide in reformed gas, hydrogen, and the oxygen in oxygen content gas.

[Claim 4] The hydrogen refiner according to claim 3 characterized by changing the amount of supply of oxygen content gas corresponding to the temperature rise of a catalyst object.

[Claim 5] The hydrogen refiner according to claim 1 or 2 characterized by using for heating of the downstream of said catalyst object reformed gas before installing a catalyst object in a reaction chamber, installing reformed gas passage in the location approached or stuck through the septum with said catalyst object and passing a cooling means.

[Claim 6] The hydrogen refiner according to claim 5 considered as the configuration which the flow of the reformed gas which passes a catalyst object, and said reformed gas before passing a cooling means counters mutually.

[Claim 7] The hydrogen refiner according to claim 5 or 6 characterized by installing a reaction chamber in the periphery section of the reformed gas passage before passing a catalyst object.

[Claim 8] The hydrogen refiner according to claim 6 or 7 characterized by having installed the catalyst object in the interior of the reaction chamber which has the tubular structure, and installing the passage of reformed gas before passing a cooling means in the periphery section of said reaction chamber.

[Claim 9] The hydrogen refiner according to claim 8 characterized by connecting two or more reaction chambers to juxtaposition.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0007

[Method of Amendment] Deletion

[Procedure amendment 3]

[Document to be Amended] Specification

[Item(s) to be Amended] 0008

[Method of Amendment] Deletion

[Procedure amendment 4]

[Document to be Amended] Specification

[Item(s) to be Amended] 0009

[Method of Amendment] Modification

[Proposed Amendment]

[0009] Moreover, as for a heating means, it is effective to use heat of reaction with the carbon monoxide in reformed gas, hydrogen, and the oxygen in oxygen content gas.

[Procedure amendment 5]

[Document to be Amended] Specification

[Item(s) to be Amended] 0010

[Method of Amendment] Modification

[Proposed Amendment]

[0010] Moreover, it is effective to change the amount of supply of oxygen content gas corresponding to the temperature rise of a catalyst object.

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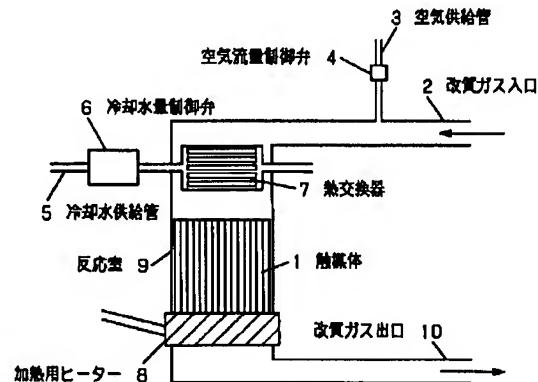
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(54)【発明の名称】 水素精製装置

(57)【要約】

【課題】 二酸化炭素と微量の一酸化炭素を含み、水素を主成分とする改質ガス中の一酸化炭素を高効率、かつ安定に酸化除去すること。

【解決手段】 改質ガスの流れ方向に対して触媒体の上流側に、触媒体もしくは改質ガスを冷却する冷却手段を備えるとともに、触媒体下流部を加熱する加熱手段を有する。



【特許請求の範囲】

【請求項1】 水素ガスを主成分とし二酸化炭素と一酸化炭素とを含有する改質ガスの供給部と、酸素含有ガスの供給部と、前記改質ガスの供給部と前記酸素含有ガスの供給部との下流側に具備した触媒体と、前記改質ガスの流れ方向に対して前記触媒体の上流側に備えた前記触媒体もしくは前記改質ガスを冷却する冷却手段と、前記触媒体の下流部を加熱する加熱手段とを有することを特徴とする水素精製装置。

【請求項2】 触媒体は、上流側と下流側とを別種の触媒で構成し、下流側の触媒が上流側の触媒よりも低温で活性を有することを特徴とする請求項1記載の水素精製装置。

【請求項3】 触媒体を複数箇所に配列し、前記触媒体に対し、空気供給部を個々に設置したことを特徴とする請求項1または2記載の水素精製装置。

【請求項4】触媒体は、ハニカム構造もしくは連通孔を有する発泡体構造の担体基材に触媒を担持したことを特徴とする請求項1、2または3記載の水素精製装置。

【請求項5】 担体基材は、金属基材であることを特徴とする請求項4記載の水素精製装置。

【請求項6】 加熱手段は、改質ガス中の一酸化炭素、水素、及び酸素含有ガス中の酸素との反応熱を用いることとを特徴とする請求項1、2、3、4または5記載の水素精製装置。

【請求項7】 触媒体の下流部温度を上流部よりも高温にすることを特徴とする請求項1、2、3、4、5または6記載の水素精製装置。

【請求項8】 酸素含有ガスの供給量を、触媒体の温度上昇に対応して変化させることを特徴とする請求項7記載の水素精製装置。

【請求項9】 触媒体を反応室内に設置し、前記触媒体とは隔壁を介して近接もしくは密着した場所に改質ガス流路を設置し、冷却手段を通過する前の改質ガスを、前記触媒体の下流部の加熱に用いることを特徴とする請求項1、2、3、4または5記載の水素精製装置。

【請求項10】 触媒体を通過する改質ガスと、冷却手段を通過する前の前記改質ガスの流れが互いに対向する構成とした請求項9記載の水素精製装置。

【請求項 11】 触媒体を通過する前の改質ガス流路の外周部に、反応室を設置したことを特徴とする請求項 9 または 10 記載の水素精製装置。

【請求項12】 管状構造を有する反応室内部に触媒体を設置し、前記反応室の外周部に、冷却手段を通過する前の改質ガスの流路を設置したことを特徴とする請求項10または11記載の水素精製装置。

【請求項13】 複数の反応室を並列に接続したことを特徴とする請求項12記載の水素精製装置。

【発明の詳細な説明】

[0 0 0 1]

【発明の属する技術分野】本発明は、燃料電池等の燃料に用いる水素を主成分とし、二酸化炭素と微量の一酸化炭素を含有する改質ガス中の一酸化炭素除去する水素精製装置に関する。

{0002}

【従来の技術】燃料電池は水素源として、炭化水素もしくはアルコールの改質によって得られる改質ガスを用いる。燃料電池のうち、100°C以下の低温で動作する固体高分子型燃料電池は、電極に用いる白金触媒が改質ガスに含まれる一酸化炭素によって被毒される。白金触媒が被毒されると、燃料電池の発電効率が著しく低下するため、一酸化炭素を100 ppm以下、好ましくは10 ppm以下に除去する必要がある。そこで改質ガスに酸素含有ガスを混合し、一酸化炭素を選択的に酸化する触媒を用い、大過剰の水素中に含まれる微量の一酸化炭素を除去する方法がとられる。一酸化炭素を効率よく除去するためには、触媒を最適温度に保持する必要があるが、改質ガスは一酸化炭素選択酸化反応の最適温度よりも高温であるため、通常、一酸化炭素を選択酸化する触媒に供給する前に冷却し、最適温度に調節する必要がある。

[0003]

【発明が解決しようとする課題】改質ガス中の一酸化炭素を選択酸化する反応では、酸素量を一酸化炭素量と同じか数倍程度とする。このとき、改質ガス中に多量に存在する水素の酸化に、酸素が消費されてしまうと、酸素不足の分だけ一酸化炭素が反応せずに排出される。このとき、反応温度が低温になるほど一酸化炭素の酸化に使用される酸素の割合は高くなる。しかし、一酸化炭素の酸化が可能な触媒活性化温度以下になると、一酸化炭素が反応せずに排出される。そこで、一酸化炭素が反応し、かつ水素の反応があまり起こらない温度領域に触媒温度を制御する必要がある。

【0004】最も一酸化炭素を効率よく酸化できる温度は、一酸化炭素の反応が起こる低温限界の温度である。しかし、一酸化炭素の選択酸化触媒の温度制御を、供給する改質ガスもしくは触媒体の冷却のみでに制御した場合、わずかに温度が低下しただけで、膨大な一酸化炭素が排出される。このため、改質ガスの流量や触媒体の温度変動を考慮して、低温限界よりも数°Cから数十°C程度高い温度領域で制御する。これにより従来の方法では、一酸化炭素酸化の選択率が低いものであった。

[0005]

【課題を解決するための手段】本発明はこのような水素精製装置の課題を考慮し、一酸化炭素を高い選択率で酸化除去でき、かつ温度制御が容易で安定に動作する水素精製装置を提供することを目的とする。そのため、本発明の水素精製装置は、水素ガスを主成分とした二酸化炭素と一酸化炭素とを含有する改質ガスの供給部と、酸素含有ガスの供給部と、前記改質ガスの供給部と前記酸素含有ガスの供給部と、

有ガスの供給部との下流側に具備した触媒体と、前記改質ガスの流れ方向に対して前記触媒体の上流側に備えた前記触媒体もしくは前記改質ガスを冷却する冷却手段と、前記触媒体の下流部を加熱する加熱手段とを有することを特徴とする水。

【0006】このとき、触媒体は、上流側と下流側とを別種の触媒で構成し、下流側の触媒が上流側の触媒よりも低温で活性を有することが有効である。

【0007】また、触媒体を複数箇所に配列し、前記触媒体に対し、空気供給部を個々に設置したことが有効である。

【0008】また、触媒体は、ハニカム構造もしくは連通孔を有する発泡体構造の担体基材に触媒を担持したことが有用である。

【0009】このとき、担体基材は、金属基材であることが有用である。また、加熱手段は、改質ガス中の一酸化炭素、水素、及び酸素含有ガス中の酸素との反応熱を用いることが有効である。

【0010】このとき、触媒体の下流部温度を上流部よりも高温にすることが有効である。また、酸素含有ガスの供給量を、触媒体の温度上昇に対応して変化させることが有効である。

【0011】また、触媒体を反応室内に設置し、前記触媒体とは隔壁を介して近接もしくは密着した場所に改質ガス流路を設置し、冷却手段を通過する前の改質ガスを、前記触媒体の下流部の加熱に用いることが有効である。

【0012】このとき、触媒体を通過する改質ガスと、冷却手段を通過する前の前記改質ガスの流れが互いに対向する構成とした。

【0013】また、触媒体を通過する前の改質ガス流路の外周部に、反応室を設置したことを特徴とする。

【0014】さらに、管状構造を有する反応室内部に触媒体を設置し、前記反応室の外周部に、冷却手段を通過する前の改質ガスの流路を設置したことを特徴とする。

【0015】また、複数の反応室を並列に接続したことを特徴とする。

【0016】

【実施の形態】上記の課題を解決するために、本発明の水素精製装置では、改質ガスの流れ方向に対して触媒体の上流側に触媒体もしくは改質ガスを冷却する手段を備えるとともに、触媒体の下流部を加熱する手段を有することを特徴としている。また、触媒体下流部の加熱に一酸化炭素と水素の酸化熱、もしくは冷却前の改質ガスを加熱に用いることを特徴としている。

【0017】本発明によると、一酸化炭素選択酸化触媒を安定して動作させることができるとともに、温度制御が著しく容易になる。

【0018】以下、本発明の実施の形態について、図面を参照して説明する。

(実施の形態1) 図1は本発明の第1の実施の形態である水素精製装置の構成略図である。図1において、1は触媒体、2は改質ガス入口、3は空気供給管、4は空気流量制御弁、5は冷却水供給管、6は冷却水量制御弁、7は熱交換器、8は加熱用ヒーター、9は反応室、10は改質ガス出口である。

【0019】次に本実施の形態の動作と特性について説明する。燃料を水蒸気改質した場合、一酸化炭素濃度は反応温度が高くなるほど上昇する。メタノールの様に300°C以下で改質する場合には、一酸化炭素濃度は1%程度となるため、改質ガスを直接改質ガス入口2から導入する。一方、反応に600°C程度の温度を要するメタン、もしくは天然ガスの改質ガスは、水性ガスシフト反応の平衡から一酸化炭素を10%以上も含んでいるため、変成触媒により水蒸気と反応させ二酸化炭素と水素に転換し、このように一酸化炭素濃度を1%以下に低減してから、改質ガス入口2から導入する。

【0020】改質ガス中の一酸化炭素を酸化するためには、空気供給管3より空気を導入し、触媒体1で反応させる。空気量が少ないと一酸化炭素が充分反応せず、逆に空気量が多いと水素の消費量が多くなるため、体積比で一酸化炭素の1~3倍の酸素が含まれるように、空気流量制御弁4で供給する空気量を調節する。空気を混合した改質ガスは熱交換器7で触媒の活性化温度すなわち一酸化炭素への触媒活性が急減し始める温度、もしくはそれ以下まで冷却され、触媒体1に供給される。

【0021】ここで、触媒体1には、白金をアルミナに担持したものをセラミックハニカムにコーティングして用いており、図2の様な特性を示す。すなわち、改質ガス中の一酸化炭素は水素よりも低温で反応するため、触媒温度を低温にするほど排出される一酸化炭素濃度が低下する。さらに温度を低下させると、触媒の活性化温度を下回るため、一酸化炭素も反応しなくなり、排出される一酸化炭素濃度は急増する。

【0022】触媒体1の上流部を熱交換器7の冷却作用で触媒の活性化温度付近、もしくは活性化温度以下になるようにしており、下流部に行くに従って温度が上昇するように触媒体1の温度を制御してあるため、触媒体1上に、一酸化炭素が最も効率よく反応する温度の帯域を作ることができる。こうして、固体高分子型燃料電池の特性を低下させない濃度である数ppmレベルまで改質ガス中の一酸化炭素を低減することができる。このとき、改質ガスや冷却装置に多少の温度変動があっても一酸化炭素が最も効率よく反応する温度の帯域の位置が上流側もしくは下流側に移動するだけで、安定に一酸化炭素を除去することができる。

【0023】本実施の形態では、酸素含有ガスとして空気を用いたが、純酸素を用いると改質ガスの水素濃度の低下が窒素を含まない分だけ緩和され、後に接続する燃料電池の発電効率は上昇する。しかしながら、通常空気

を用いた方がコスト的には有利である。

【0024】また、本例では触媒体1の加熱に電気ヒーターを用いたが、一酸化炭素、及び水素の酸化熱を用いて、触媒体1の下流部の加熱手段としてもよい。触媒体1を通過する改質ガスの流量、空気の割合を調節し、一酸化炭素と水素の酸化熱を用いることによって、電気ヒーターなどを用いることなく、もしくは最小限のヒーター加熱で、触媒体1の温度分布を最適にすることができます。

【0025】また、空気量に比例して、CO、水素の酸化熱が増えるので、空気量を調節することで、触媒体1の温度を適切な状態に保つこともでき、この方法で、より安定に触媒体1を機能させることができます。

【0026】また、触媒体1の担体基材にコーチェライトハニカムを用いたが、金属基材を用いてもよい。担体基材に金属基材を用いることによって、反応熱を速やかに逃がすことができため、一酸化炭素と水素の酸化熱による温度上昇の抑制が可能である。従って、触媒体1の単位体積あたりの改質ガス処理量を上げることができますとともに、負荷変動による反応熱増減の影響も緩和され、安定な特性が得られる。

【0027】(実施の形態2) 本発明の第2の実施の形態について説明する。本例の水素精製装置は図3に示すように、管状の反応室18の内部にハニカム形状の触媒体11を設置し、反応室18の外側に改質ガスの流路を設け、触媒体11の下流部と接する改質ガス流路の壁面には熱交換用フィン20が設けてあるものであり、作用効果の大部分は実施の形態1と類似である。したがって異なる点を中心で本例を説明する。

【0028】図3は本例の断面構成図である。触媒体11の下流部の周囲側壁に近接して熱交換用フィン20を設けることにより、触媒体11の下流部を加熱することができるとともに、改質ガスを冷却でき、熱交換器17での冷却が容易になる。また、改質ガスの流路が触媒体11を保溫するため、触媒体11の中心部と外周部の温度分布が均一化され、効率よく一酸化炭素の酸化を行うことができる。また、触媒体11を通過する改質ガスと、熱交換器17を通過する前の改質ガスの流れが対向するように構成しているため、高温の改質ガスが触媒体1の下流部と熱交換し、冷却された改質ガスが触媒体上流部の側面を通過するため、触媒体1の上流部温度を低く、下流部温度を高くでき、一酸化炭素の選択酸化に対して最適な温度分布にすることができます。

【0029】本例では、反応室18が1本である例を示したが、反応室18を複数設けることもできる。反応室18を複数設けることによって、改質ガスとの熱交換の効率を高めることができ、また、大容量化にも対応できるものである。

【0030】(実施の形態3) 本発明の第3の実施の形態である水素精製装置について説明する。本例は図4に

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示すように、管状の改質ガス流路の外周に反応室28を設け、反応室28の内部にハニカム形状の触媒体21を設置し、触媒体21の下流部と接する改質ガス流路の壁面には熱交換用フィン30が設けてあるものであり、作用効果の大部分は実施の形態2と類似である。したがって異なる点を中心で本例を説明する。

【0031】図4は本例の水素精製装置の断面構成図である。触媒体21の下流部と近接する改質ガス流路の壁面に熱交換用フィン30を設けることにより、触媒体21の下流部を加熱することができるとともに、改質ガスを冷却でき、熱交換器27での冷却が容易になる。また、改質ガスの流量を大きくする場合など、一酸化炭素と水素の酸化熱による温度上昇が大きい場合には、時として熱交換器による冷却だけでは不足する場合がある。反応室38の外周部から放熱させる構成とすることにより、触媒体21の温度上昇を抑制することができるため、改質ガスの流量を増加させて負荷を大きくした場合にも対応できるものである。

【0032】(実施の形態4) 本発明の第4の実施の形態について説明する。本例の水素精製装置は図5に示すように、反応室40の内部にハニカム形状の第一触媒体31と、第一触媒体31の下流側に第二触媒体32を設置するものであり、作用効果の大部分は実施の形態1と類似である。したがって異なる点を中心で本実施の形態を説明する。

【0033】図5は本実施例の水素精製装置の断面構成図である。一酸化炭素選択触媒は触媒に含まれる貴金属種、担体の種類などによって機能する温度領域が異なる。第一触媒体31には高温用触媒を用い、第二触媒体32には低温用触媒を用いる。具体的には第一触媒体31に白金をゼオライトに担持したものを用い、第二触媒体32に白金をアルミナに担持したものを用いた。

【0034】図6に示したように、第一触媒体31に用いている高温用触媒は、高温では一酸化炭素を高選択率で酸化し、低温では反応せず一酸化炭素とともに未反応の酸素を通過させる。したがって、高温では第二触媒体32に酸素が供給されないため、全く反応に関与しない。一方、低温では一酸化炭素と酸素が第一触媒体31を通過するため、第二触媒体32が主に機能し一酸化炭素を除去することができる。また、第二触媒体32での反応熱によって、第一触媒体31の下流部を加熱でき、第一触媒体31の温度分布を最適な状態にすることができます。このように、異なる温度領域で機能する複数の触媒体を配列することにより、広い温度範囲で触媒体を機能させることができるものである。

【0035】本例では、2個のハニカム形状の触媒体を配列した例を示したが、3個以上の触媒体を配列してもよい。数多くの触媒体を配列することにより、広い温度範囲で効率よく一酸化炭素を除去することができる。

【0036】また、第一触媒体31と第二触媒体32を

分離せず、一体化した構成にしてもよい。一体構成することにより、特にペレット状の触媒体を用いたときに、装置への組み込みが容易になる。

【0037】また、第二触媒体32に一酸化炭素を水素と反応させてメタン化する触媒を用いてもよい。第一触媒体31で酸素をすべて消費する温度に制御した場合、残留した一酸化炭素は、酸素が無いため第二触媒体32で酸化することはできない。第二触媒体32に一酸化炭素をメタン化する触媒を用いることにより、一酸化炭素を水素と反応させてメタンに転換することができる。また、一酸化炭素のメタン化反応は、一酸化炭素選択酸化反応よりも高温で進行しやすいため、本実施例のように第二触媒体の下流部に加熱用ヒーター39を設置するところが好ましい。

【0038】(実施の形態5) 本発明の第5の実施の形態について説明する。本例の水素精製装置は図7に示すように、反応室62の内部にハニカム形状の第一触媒体51と、第一触媒体51の下流側に第二触媒体52を設置し、第一触媒体51と第二触媒体52の間に第二空気供給管55を設置したものであり、作用効果の大部分は実施の形態1と類似である。したがって異なる点を中心にして本実施例を説明する。

【0039】図7は本例の水素精製装置の断面構成図である。第一触媒体51には低温用触媒を用い、第二触媒体52には高温用触媒を用いる。第一触媒体51で反応による温度上昇が大きい場合、時として一酸化炭素酸化の選択性が低下する。このため、第二触媒体52と第二空気供給管55を設け、第一空気供給管54からの第一触媒体51への空気供給を減らし、第一触媒体51での温度上昇を抑制する。これによって、効率よく一酸化炭素を除去することができる。

【0040】大部分の一酸化炭素は第一触媒体51で除去できる。しかし、空気供給量を減らすことによって、排出される一酸化炭素濃度が、空気供給量を減らさない場合に比べて多少増加する。このため、第二触媒体52に残った一酸化炭素に対応する量の空気を供給し、残りの一酸化炭素を除去する。第一触媒体51で温度上昇が抑制された分だけ一酸化炭素酸化の選択性は向上するため、第一触媒体51と第二触媒体52に対する必要な空気の総量は減少する。また、第二触媒体52への酸素含有ガスの供給量が少なく、酸化熱による温度上昇が小さいため、第二触媒体52を最適温度に保つには、加熱用ヒーター61で加熱する。このようにして、効率よく安定に一酸化炭素を除去することができる。

【0041】本例では、第一触媒体51に低温用触媒を用い、第二触媒体52に高温用触媒を用いたが、逆に第一触媒体51に高温用触媒を用い、第二触媒体52に低温用触媒を用いてもよい。第一触媒体51に高温用触媒を用いることによって、熱交換器60における冷却負荷を減らすことができる。また、第二触媒体52に低温用

触媒体を用いることによって、第一触媒体51から第二触媒体52の間での放熱による温度低下が大きい場合でも、一酸化炭素を効率よく除去することができる。

【0042】以上、本発明について、メタン改質ガス、及びメタノール改質ガスを用いた水素精製装置に実施した例で説明したが、本発明はこれに限定されるものではないことは勿論である。すなわち、以下のような場合も本発明に含まれる。

【0043】本実施の形態では、プロパン、ブタンなど、他の気体系炭化水素燃料でも、ガソリン、灯油などの液体系炭化水素燃料の改質ガスでもよい。

【0044】また、触媒体には、主として白金をアルミナに担持したものを触媒として用いたが、一酸化炭素に対して選択性に酸化反応を行うことができる触媒であれば、ロジウム、ルテニウムなど、他の貴金属や、これらを複合化させた触媒、またはペロブスカイト構造をもつ遷移金属複合酸化物などを用いてもかまわない。また、アルミナの代わりにシリカアルミナやゼオライトなどを用いてもかまわない。また、場合によっては一酸化炭素を選択性にメタン化する触媒を用いてもよい。

【0045】また、触媒体1の形状はハニカム形状としたが、改質ガスが効率よく触媒に接触し、圧力損失があまり大きくならない形状であれば、球状でもペレット状のものでもよい。

【0046】また、改質ガスの冷却には水を流通させて熱交換させる方法を用いたが、温度によって必要であれば沸点の高いエチレンギリコールのようなオイル状物質、もしくはこれらの混合液を流通させてもかまわない。また、改質部へ供給する気体を用い、改質原料ガスの予熱に用いてもかまわない。

【0047】

【実施例】(実施例1) 白金を担持したアルミナを直径50mm、長さ100mmのコーチェライトハニカムにコーティングして触媒体1を作製した。この触媒体1を図1に示す水素精製装置の反応室9の中に設置し、一酸化炭素1%、二酸化炭素を15%、水蒸気15%、残りが水素である改質ガスを、改質ガス入口2より、毎分10リットルの流量で導入した。空気供給管からは、毎分1リットルの空気を供給した。この空気を混合させた改

質ガスを、中に水を流通させた熱交換器7で100°Cまで低下させ、触媒体1で反応させた。触媒体1の下流側は加熱用ヒーター8を用いて、150°Cとなるように設定した。触媒体1の温度分布を測定すると、上流部から下流部にかけて、ほぼ直線的に温度が上昇していた。触媒体1通過後の改質ガス出口10から排出される改質ガスの組成をガスクロマトグラフィで測定したところ、一酸化炭素濃度は5ppmであった。また、熱交換器7の中を流れる水の流量を変え、改質ガス温度を90°C、80°Cと変化させたところ、一酸化炭素濃度はそれぞれ6ppm、9ppmとなつた。また、加熱ヒーター8の設

定温度を変え、触媒体1下流部の温度を140°C、160°Cにしたところ、一酸化炭素濃度はそれぞれ4 ppm、9 ppmとなった。

【0048】(実施例2)実施例1で作製した触媒体を図3に示す反応室18内に設置し、改質ガスを改質ガス入口12より導入した。改質ガス入口12での改質ガス温度を測定したところ、200°Cであった。熱交換用フィン20を通じて加熱された触媒体11下流部の温度を測定したところ、150°Cであった。熱交換器17で改質ガスを100°Cまで低下させ、触媒体11で反応させたところ、一酸化炭素濃度は5 ppmであった。

【0049】(実施例3)図4に示すように、直径100mm、長さ100mmのコーチェライトハニカムの中心に直径80mmの穴をくりぬいたものに、実施例1と同じく触媒をコーティングし、触媒体21を作製した。熱交換用フィン30を通じて加熱された触媒体11下流部の温度を測定したところ、150°Cであった。熱交換器27で改質ガスを100°Cまで低下させ、触媒体21で反応させたところ、一酸化炭素濃度は4 ppmであった。

【0050】(実施例4)白金を担持したモルデナイトを直径50mm、長さ50mmのコーチェライトハニカムにコーティングして第一触媒体31、白金を担持したアルミナを直径50mm、長さ50mmのコーチェライトハニカムにコーティングして第二触媒体32をそれぞれ作製した。この第一触媒体31、第二触媒体32をそれぞれ図5に示すように反応室40内に設置した。改質ガスは熱交換器38で140°Cまで冷却し、第二触媒体32の下流部を160°Cになるように加熱用ヒーター39で制御した。第一触媒体31の下流部の温度を測定すると150°Cであった。改質ガス出口41の一酸化炭素濃度を測定したところ、1 ppmであった。

【0051】(実施例5)白金を担持したモルデナイトを直径50mm、長さ50mmのコーチェライトハニカムにコーティングして第一触媒体51、白金を担持したアルミナを直径50mm、長さ50mmのコーチェライトハニカムにコーティングして第二触媒体52をそれぞれ作製した。この第一触媒体51、第二触媒体52をそれぞれ図7に示すように反応室62内に設置した。改質ガスは熱交換器60で150°Cまで冷却し、第二触媒体52の下流部を130°Cになるように加熱用ヒーター61で制御した。第一触媒体51の下流部の温度は測定すると140°C、第二触媒体上流部の温度は100°Cであった。改質ガス出口63の一酸化炭素濃度を測定したところ、2 ppmであった。

【0052】(比較例1)実施例1において、加熱ヒーター8を取り去り、同じく改質ガスを改質ガス入口2より導入した。熱交換器7によって改質ガス温度を100°Cまで低下させ、触媒体1で反応させた。触媒体1の温度分布を測定したところ、上流部が100°Cで下流に行

くに従って直線的に温度が低下し、最下流部温度は90°Cであった。触媒体1通過後の改質ガス出口10から排出される改質ガスの組成をガスクロマトグラフィで測定したところ、2000 ppmであった。また、熱交換器7の中を流れる水の流量を変え、改質ガス温度を90°C、110°C、120°Cと変化させたところ、一酸化炭素濃度はそれぞれ5000 ppm、200 ppm、500 ppmとなった。

【0053】(比較例2)実施例5において、加熱用ヒーター61を取り外したところ、第一触媒体51の下流部の温度は測定すると140°C、第二触媒体52上流部の温度は100°C、第二触媒体52下流部の温度は90°Cであった。改質ガス出口63の一酸化炭素濃度を測定したところ、500 ppmであった。

【0054】

【発明の効果】以上述べたところから明らかのように、本発明によると、一酸化炭素選択酸化触媒を安定して動作させることができるとともに、温度制御が著しく容易になる。

20 【図面の簡単な説明】

【図1】本発明の第1の実施の形態である水素精製装置の断面構成を示した図

【図2】本発明の第1の実施の形態である水素精製装置における一酸化炭素選択酸化触媒の作動温度と触媒通過後の一酸化炭素濃度の関係を示した図

【図3】本発明の第2の実施の形態である水素精製装置の断面構成を示した図

【図4】本発明の第3の実施の形態である水素精製装置の断面構成を示した図

30 【図5】本発明の第4の実施の形態である水素精製装置の断面構成を示した図

【図6】本発明の第4の実施の形態である水素精製装置における高温用触媒と低温用触媒の作動特性を示した図

【図7】本発明の第5の実施の形態である水素精製装置の断面構成を示した図

【符号の説明】

1, 11, 21 触媒体

2, 12, 22, 33, 53 改質ガス入口

3, 13, 23, 34 空気供給管

40 4, 14, 24, 35 空気流量制御弁

5, 15, 25, 36, 58 冷却水供給管

6, 16, 26, 37, 59 冷却水量制御弁

7, 17, 27, 38, 60 热交換器

8, 39, 61 加熱用ヒーター

9, 18, 28, 40, 62 反応室

10, 19, 29, 41, 63 改質ガス出口

20, 30 热交換用フィン

31, 51 第一触媒体

32, 52 第二触媒体

50 54 第一空気供給管

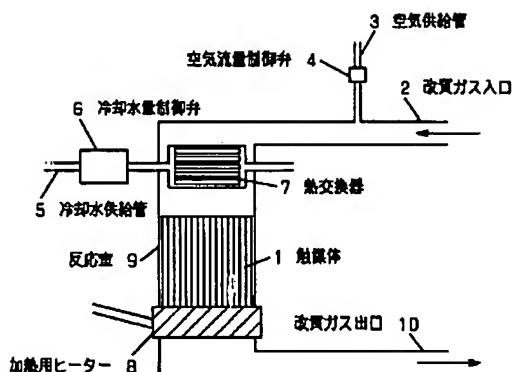
55 第二空気供給管

56 空気流量第一制御弁

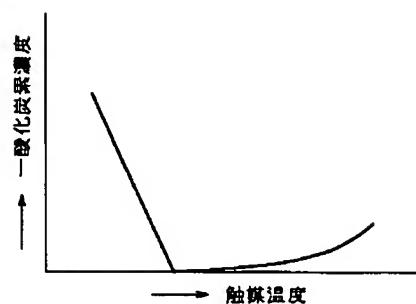
* 57 空気流量第二制御弁

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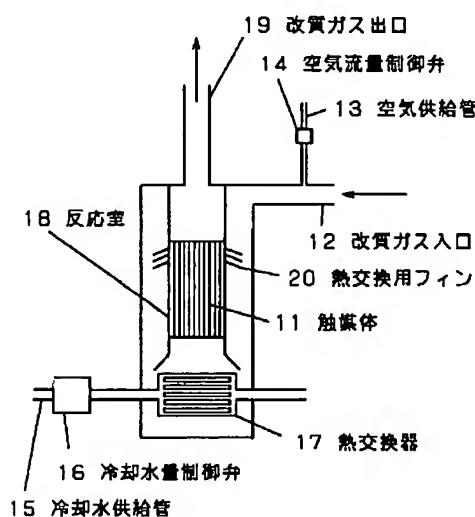
【図1】



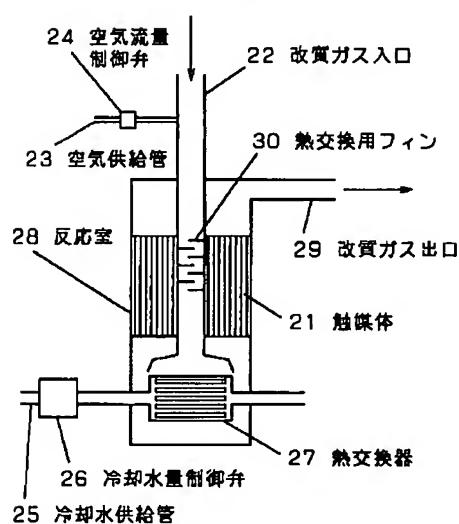
【図2】



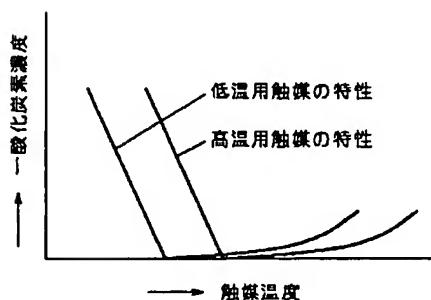
【図3】



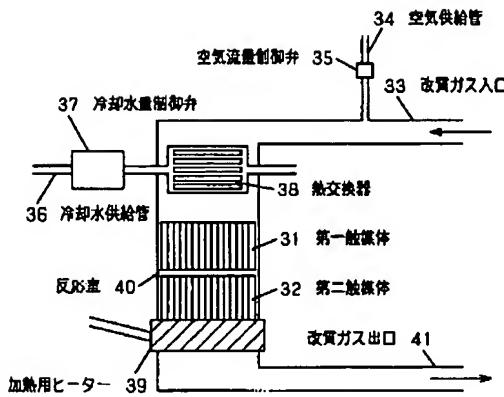
【図4】



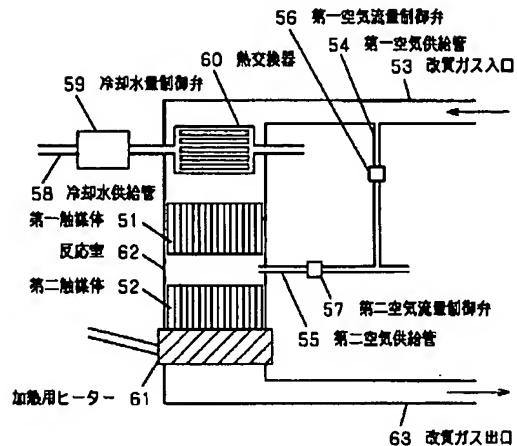
【図6】



【図5】



【図7】



フロントページの続き

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【手続補正書】

【提出日】平成14年6月4日(2002.6.4)

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】特許請求の範囲

【補正方法】変更

【補正内容】

【特許請求の範囲】

【請求項1】 水素ガスを主成分とし二酸化炭素と一酸化炭素とを含有する改質ガスの供給部と、酸素含有ガスの供給部と、前記改質ガスの供給部と前記酸素含有ガスの供給部との下流側に具備した触媒体と、前記改質ガスの流れ方向に対して前記触媒体の上流側に備えた前記触媒体もしくは前記改質ガスを冷却する冷却手段と、前記触媒体の下流部を加熱する加熱手段とを有することを特徴とする水素精製装置。

【請求項2】 触媒体は、上流側と下流側とを別種の触媒で構成し、下流側の触媒が上流側の触媒よりも低温で活性を有することを特徴とする請求項1記載の水素精製装置。

【請求項3】 加熱手段は、改質ガス中の一酸化炭素、水素、及び酸素含有ガス中の酸素との反応熱を用いることを特徴とする請求項1または2記載の水素精製装置。

【請求項4】 酸素含有ガスの供給量を、触媒体の温度上昇に対応して変化させることを特徴とする請求項3記載の水素精製装置。

【請求項5】 触媒体を反応室内に設置し、前記触媒体とは隔壁を介して近接もしくは密着した場所に改質ガス流路を設置し、冷却手段を通過する前の改質ガスを、前記触媒体の下流部の加熱に用いることを特徴とする請求項1または2記載の水素精製装置。

【請求項6】 触媒体を通過する改質ガスと、冷却手段を通過する前の前記改質ガスの流れが互いに対向する構

成とした請求項5記載の水素精製装置。

【請求項7】 触媒体を通過する前の改質ガス流路の外周部に、反応室を設置したことを特徴とする請求項5または6記載の水素精製装置。

【請求項8】 管状構造を有する反応室内部に触媒体を設置し、前記反応室の外周部に、冷却手段を通過する前の改質ガスの流路を設置したことを特徴とする請求項6または7記載の水素精製装置。

【請求項9】 複数の反応室を並列に接続したことを特徴とする請求項8記載の水素精製装置。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0007

【補正方法】削除

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0008

【補正方法】削除

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0009

【補正方法】変更

【補正内容】

【0009】また、加熱手段は、改質ガス中の一酸化炭素、水素、及び酸素含有ガス中の酸素との反応熱を用いることが有効である。

【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0010

【補正方法】変更

【補正内容】

【0010】また、酸素含有ガスの供給量を、触媒体の

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温度上昇に対応して変化させることが有効である。